DIELECTRIC CONSTANTS AND MOLECULAR STRUCTURE

Part II. Relationship of the New Equation to Previous Equations

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The failure of the Debye-Clausius-Mosotti equation in explaining the temperature variation of the high dielectric constant of pure liquids and solids is well known. The limited applicability of the D.C.M. equation to dilute solutions in nonpolar solvents also leads to the so called solvent effect.

A most general and extraordinarily simple relationship between dielectric constant and dipole moment, has been shown[18] to be

$$\frac{(\epsilon - n^2)\,M}{d} = \frac{4\pi N\mu^2}{3kT}\,\frac{(j+1)}{j},$$

where $j = \infty$ for gases and $\frac{1}{2}$ for solids and liquids. The theoretical derivation of this equation follows from the considerations of quantised orientations similar to those applied in the magnetic case. These are also inherent in previous theories of *hindered rotation*, parallel and anti-parallel orientations postulated by Debye. Debye[4] has shown that the binding forces between molecules become of such magnitude that molecular rotation is restricted and the liquid assumes a quasi-crystalline character. A study of the electric double refraction (Kerr effect) shows very clearly that even in the case of nonpolar liquids the free rotation is considerably inhibited. Interference maxima in the scattering of X-rays by liquids indicate that orientations of molecules in liquids are similar to that in solids. The scattering of light shows the similarity between the liquids and the crystals not only in the orientation but also in the types of allowed molecular motions. Brillouin's calculations reveal that the motions of neighbouring molecules are strongly coupled in liquids, just as in solid bodies. "Altogether one can conclude with complete certainty that the orientation and the coupling of molecules in liquids are very similar to the binding of molecules in solid crystals."[4]

The D.C.M. equation which is based on completely free rotation cannot therefore be applied to liquids and solutions.

In considering the high dielectric constant of ice and other solids Debye introduced the postulate of parallel and antiparallel orientations in solids and suggested that the orientation term is given by μ^2/kT.[5] The derivation of this term by both the classical and quantum methods has already been given. Debye[3] has also suggested $\mu^2/2kT$ for orientation polarisation. This happens when j in the new equation is equal to 2.

Although the classical method of treatment is open to criticism it gives us a picture of the model. Hence the derivation of $\mu^2/2kT$ is given by this method.

The basis of the consideration of a long thin cylindrical cavity with its axis parallel to the field in evaluating the internal field was on the assumption that a dipole corresponds to a long thin rod which can orient itself in the line of the field, along or opposite to it. In this case it is to be assumed that the mechanism of electric polarisation is caused by the occasional crossing over of a potential barrier by the dipole. The assumption of such a cavity is justified in the case of solids and pure polar liquids where the dipoles are crowded and hence the equilibrium position of the dipole could be either along or opposite the line of the field. When, however, the case of dilute solutions of polar substances in non-polar media is considered it is obvious that in fairly dilute region the dipole is sufficiently separated mutually so as to be able to completely turn over by scooping out a disc-like cavity, a consideration of which is thus be taken into account in evaluating the internal field in order to derive an expression for molecular polarisation in such a case.

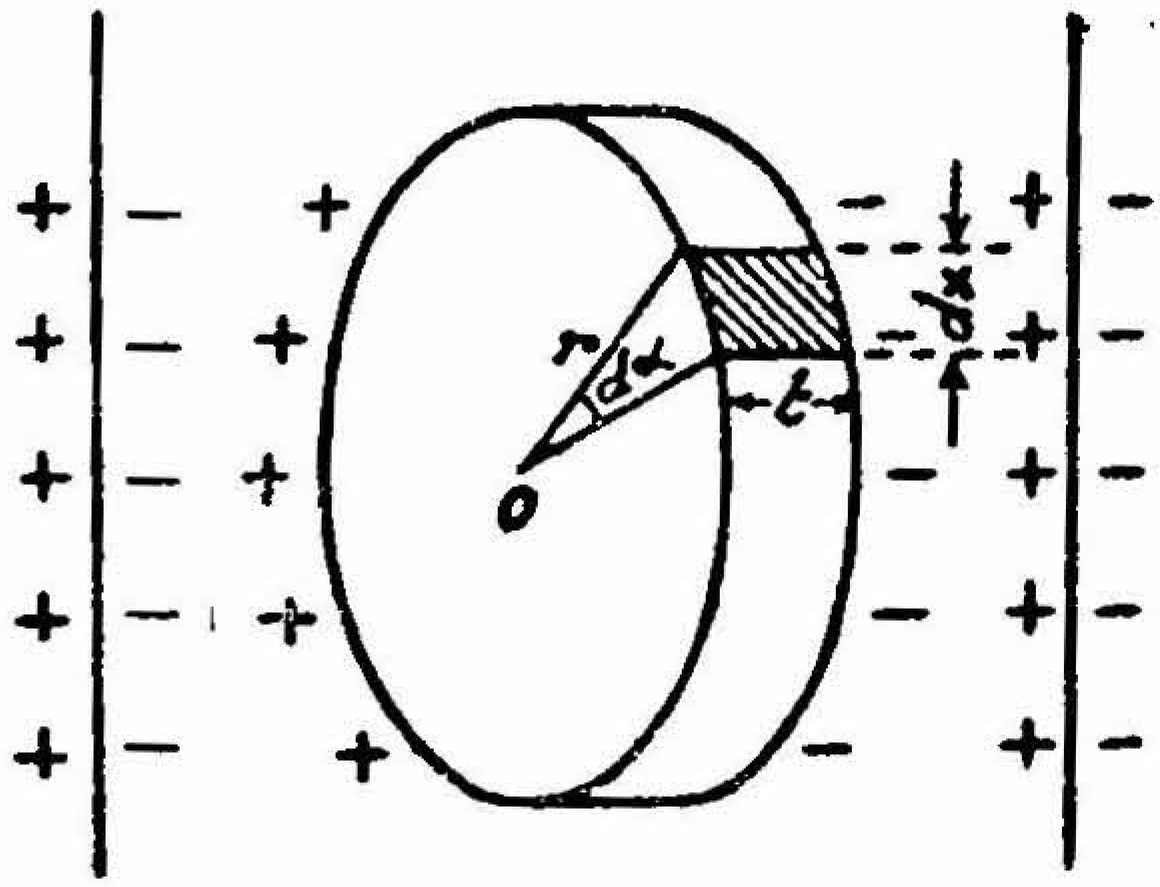

FIG. 1

As before $F = F_1 + F_2$, where $F_1 = 4\pi\sigma$ and F_2 is equal to $-4\pi I + F_2'$. F_2', the force due to the induced charge on the periphery of the disc cavity, is evaluated as follows. The area of small strip on the periphery of length 't' (the thickness of the cavity) and breadth $dx = tdx$. Its charge $= tdx\,I$. The force exerted on unit charge at 'O' the centre of the cavity parallel to the field is got by applying Coulombs' law to every strip on the periphery and integrating

$$F_2' = \int \frac{tdx\,I}{r^2} \cos\alpha,$$

where r = radius of the cavity and α = the angle between the direction of the field and the line joining the centre of the cavity with the strip considered. Since $dx = r \cdot d\alpha$ where $d\alpha$ is the angle subtended by the arc dx at O.

$$F_2' = \frac{2x\,It}{r} \int_{-\pi/2}^{+\pi/2} \cos\alpha \, d\alpha = \frac{2t\,I}{r} \left[\sin\alpha\right]_{-\pi/2}^{+\pi/2} = \frac{4t\,I}{r}.$$

Now the dipole is very thin and long so that the thickness t of the cavity scooped out by its rotation is far less than the radius r. Hence $t/r \rightarrow 0$. Thus $F_2' = 0$, as in the case of a needle cavity. Thus $F = 4\pi\sigma - 4\pi I$ from which it can be derived as before that $F = E$ and hence finally $P = (\epsilon - 1)\, M/d$. Thus the consideration of a thin disc cavity does not make any difference in the calculation of the internal field and the molecular polarisation.

In the case of the distribution of molecules with their axes in two specific directions, along and opposite the line of the field the average moment $\bar{m}$ of a molecule in the direction of the field was calculated as μ^2/kT. In the case of molecules which have sufficient freedom to execute a complete rotation in one plane the expression for $\bar{m}$ will be different. In this case when there is no field the molecules can be considered to be distributed with the same probability in the one plane. Thus the number of molecules pointing in the direction confined to an angle $d\theta$ is $A\, d\theta$ where A is a constant. In a field of intensity 'F' the number confined to the angle $d\theta$ is according to Boltzmann's law $dn = Ae^{-U/kT}\, d\theta$ where U, the potential energy of the molecule $= mF$, m being the electric moment. $U = -\mu F \cos\theta$ where μ is the absolute value of the electric moment. Hence $dn = Ae^{\mu F/kT \cos\theta}\, d\theta$. The electric moment of dn molecules at an angle θ will have a component along the field equal to $Ae^{\mu F/kT \cos\theta}\, d\theta\, \mu \cos\theta$. Thus the average moment $\bar{m}$ along the field for a single molecule

$$\bar{m} = \frac{\int_0^{2\pi} Ae^{\mu F/kT \cos\theta}\, \mu \cos\theta \; d\theta}{\int_0^{2\pi} Ae^{\mu F/kT \cos\theta}\, d\theta}$$

$$= \frac{A \int_0^{2\pi} (1 + \mu F/kT \cos\theta)\, \mu \cos\theta \; d\theta}{A \int_0^{2\pi} (1 + \mu F/kT \cos\theta)\, d\theta}$$

using $e^{\mu F/kT \cos\theta} \simeq 1 + \mu F/kT \cos\theta$, since $\mu F/kT \cos\theta << 1$

i.e., $$\bar{m} = \frac{\mu \left[\int_0^{2\pi} \cos\theta \; d\theta + \alpha \int_0^{2\pi} \cos^2\theta \; d\theta \right]}{\left[\int_0^{2\pi} d\theta + \alpha \int_0^{2\pi} \cos\theta \; d\theta \right]} \quad \text{where } \alpha = \mu F/kT$$

Since $\int_0^{2\pi} \cos\theta\, d\theta = [\sin\theta]_0^{2\pi} = 0$ and

$$\int_0^{2\pi} \cos^2\theta\, d\theta = \tfrac{1}{2}\,[\theta + \sin\theta\cos\theta]_0^{2\pi} = \pi$$

$$\bar{m} = \frac{a\mu\pi}{2\pi} = \frac{\mu a}{2} = \frac{\mu^2 F}{2kT}.$$

This differs by a factor $\frac{1}{2}$ from the expression obtained on the basis of two orientations along and opposite the field direction.

For a dipole having $(2j + 1)$ possible orientations a general expression was derived for $\bar{m}$ as $\bar{m} = \frac{\mu^3 F}{3kT}\,\frac{(j+1)}{j}$. Thus the present case of a orientation in one plane conforms with $j = 2$.

The experimental verification of the previous theories of Debye and Onsager[12] in the case of dilute solutions and pure liquids has been found to be due to *remarkable and fortuitous coincidence*, which arises from the fact that their equations arithmetically *approximate* to the correct relationship given above. The theories of Kirkwood[9] and Frōlich[6, 7] require the evaluation of *undesirable and inaccurate* parameters. Even the limited applicability of Frōlich and Sack's equation which contained two parameters was vitiated by an arithmetical error in calculation since a wrong value of N was employed.[6]

It is interesting to note that some of the relationships, between dielectric constant and dipole moment, which have been in the past found applicable under certain conditions arithmetically reduce to the form of the new relationship under the considered conditions wherein certain valid approximations could be made.

Thus the D.C.M. equation applicable to gases and vapours

$$\frac{(\epsilon - 1)}{(\epsilon + 2)}\frac{M}{d} - \frac{(n^2 - 1)}{(n^2 + 2)}\frac{M}{d} = \frac{4\pi N\mu^2}{9kT}$$

reduces itself to the form of the new equation for gases, *viz.*,

$$\frac{(\epsilon - n^2)\,M}{d} = \frac{4\pi N\mu^2}{3kT} \text{ as } \epsilon \simeq n^2 \simeq 1.$$

Wyman[17] has empirically found that for a number of liquids the polarisation per c.c. is given by $p = \frac{\epsilon + 1}{8.5}$. The complete equation can be written on the basis of such polarisation as

$$\frac{(\epsilon - n^2)\,M}{d} = \frac{4\pi N\mu^2}{kT}\,\frac{8\cdot 5}{9}$$

which is very nearly the same form as the new equation since the factor $8 \cdot 5/9 \simeq 1$. Onsager's[12] equation

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2+2)^2}\frac{M}{d} = \frac{4\pi N\mu^2}{9kT}$$

which was shown by Böttcher[1] to be applicable to a number of liquids leads to the new equation, when $2\epsilon >> n^2$ and $n^2 \simeq 2 \cdot 25$. The failure of Onsager's equation for chloroform, acetone and ethers is due to these limitations.

Frōlich and Sack[7] have proposed the following equation which has been applied to the case of a polymer, glycol phthalate

$$\epsilon = n^2 + \frac{3\epsilon}{2\epsilon + n^2}\frac{4\pi N\mu^2}{3kT}\left(1 + \tfrac{1}{3}\frac{\overline{\epsilon - n^2}^{\,2}}{\epsilon n^2}\right)\frac{d}{M},$$

where $\epsilon =$ static dielectric constant and $n^2 =$ high frequency dielectric constant. As $n^2 \simeq 2$ and

$$\frac{3\epsilon}{2\epsilon + n^2} \simeq 3/2 \textit{ i.e., } 2\epsilon >> n^2 \text{ and } (\epsilon - n^2)^2$$

$$\simeq \epsilon^2 - 2\epsilon n^2 \text{ then } (\epsilon - n^2) = \frac{4\pi N\mu^2}{kT} \cdot \tfrac{1}{2}(1 + \epsilon/6 - 2/3)\, d/M.$$

It is seen that when $\epsilon \simeq 9$ the equation approximates to the form $(\epsilon - n^2)\, M/d = 4\pi N\mu^2/kT$. Frōlich and Sack themselves have pointed out the limitations of their equation to $\epsilon < 9$. Even the limited agreement they have obtained involves the calculation of an unknown parameter μ^2/a^3kT which is done by fitting the equation to an experimental point. In a further paper Frölich[6] has presented a quantitative theory of dielectric properties of crystalline solids consisting of dipolar long-chain molecules. According to him the static dielectric constant rises with increasing temperature up to a critical temperature and then decreases. The equation derived on considerations of dipolar interaction and preferred orientation has been applied to explain the experimental dielectric constants of a solid ketone. According to this relationship the static dielectric constant ϵ is given by $\epsilon = n^2 + \dfrac{4\pi\mu_b{}^2 N}{kT}\, G\,(T/T_0)$, where $G\,(T/T_0)$ is a factor accounting for interaction and is calculable in terms of T_0; μ_b is the component of the moment of the dipole along a specified axis and is calculated on structural basis. Finally the equation assumes the form $10/3 \cdot 5\,(\epsilon - 2 \cdot 5) = T_0/T \cdot G\,(T/T_0)$. The unknown parameter T_0 has been determined by Frölich solving the equation by assuming for 'ϵ' the experimentally observed value. With the value of 'T_0' so obtained Frölich calculates the function $T_0/T \cdot G\,(T/T_0)$ as a function of temperature and finds some amount of agreement with the equivalent factor obtained experimentally, *viz.*, $(\epsilon - 2{\cdot}5)\,10/3{\cdot}5$. Daniel[2] has pointed out that Frōlich's calculation of the constant $10/3{\cdot}5$ is erroneous since a wrong value for N has been employed. In view of this error the agreement with experimental data of the theoretical relationship does not exist though it could be, as has been done by Frölich, restored by changing the other parameter μ_b.

The D.C.M. equation for dilute solutions has the form

$$P_{1,2} = \frac{(\epsilon_{1,2} - 1)}{(\epsilon_{1,2} + 2)} \frac{(M_1 f_1 + M_2 f_2)}{d_{1,2}} = P_1 f_1 + P_2 f_2$$

$$= \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \frac{M_1 f_1}{d_1} + P_2 f_2$$

or $$P_2 = \left\{ \frac{(\epsilon_{1,2} - 1)}{(\epsilon_{1,2} + 2)} \frac{(M_1 f_1 + M_2 f_2)}{d_{1,2}} - \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \frac{M_1 f_1}{d_1} \right\} \Big/ f_2$$

and $\mu = \sqrt{\dfrac{(P_{2(\infty)} - P_E)\,9kT}{4\pi N}}$ where $P_{2(\infty)}$ is P_2 extrapolated to infinite dilution $(f_2 = 0)$

According to the new equation

$$P_{1,2\,(\text{new})} = \frac{(\epsilon_{1,2} - 1)(M_1 f_2 + M_2 f_2)}{d_{1,2}} = P_1 f_1 + P_2 f_2 = \frac{(\epsilon_1 - 1)\,M_1 f_1}{d_1} + P_2 f_2$$

or $$P_{2\,(\text{new})} = \left\{ \frac{(\epsilon_{1,2} - 1)(M_1 f_1 + M_2 f_2)}{d_{1,2}} - \frac{(\epsilon_1 - 1)\,M_1 f_1}{d_1} \right\} \Big/ f_2$$

and $$\mu_{(\text{new})} = \sqrt{\frac{(P_{2\,(\text{new})} - P_{E\,(\text{new})})\,kT}{4\pi N}}$$

In dilute nonpolar solutions $(\epsilon_{1,2} + 2) \simeq 4{\cdot}5$. Hence

$P_{2\,(\text{new})} \simeq 4{\cdot}5\ P_{2(\text{D.C.M})}$ and

$$P_{E\,(\text{new})} = \frac{(n^2 - 1)\,M}{d} = (n^2 + 2)\,P_{E\,(\text{D.C.M.})} \simeq 4{\cdot}5\,P_{E\,(\text{D.C.M.})}$$

Thus $$\mu_{(\text{new})} = \sqrt{\frac{[P_{2\,(\text{D.C.M.})} - P_{E\,(\text{D.C.M.})}]\,4{\cdot}5\,kT}{4\pi N}}$$

and $$\mu_{(\text{D.C.M.})} = \sqrt{\frac{[P_{2\,(\text{D.C.M})} - P_{E\,(\text{D.C.M.})}]\,9kT}{4\pi N}}$$

It is found that $\mu_{(\text{D.C.M.})}/\mu_{(\text{new})} \simeq 1{\cdot}4$. When $P_{2(\infty)\,(\text{D.C.M.})} > P_{2\,(\text{D.C.M.})}$ observed at a particular concentration, this factor approaches unity. The well known solvent effect on HCl, HBr, etc., is due to this factor. If the solvent is polar (*i.e.*, $\epsilon_{1,2} > 2{\cdot}5$) then the ratio $\mu_{(\text{D C.M.})}/\mu_{(\text{new})}$ will be less than $1{\cdot}4$.

Three types of curves are obtained when the molecular polarisations calculated according to Debye-Clausius-Mosotti relationship are plotted against f_2 the mole fraction of solute. In the I case P_2 decreases with increasing f_2 (*e.g.*, nitrobenzene); in the II case P_2 remains constant throughout, (*e.g.*, ether) and in the III case P_2 rises with increasing f_2. These anomalous curves are usually explained on the basis of association. If however the new equation for $P = (\epsilon - 1) M/d$ is used the anomalies are rectified since the polarisation $P_{2\,(D.C.M.)}$ given by

$$\left\{\frac{(\epsilon_{1,2}-1)}{(\epsilon_{1,2}+2)}\frac{(M_1 f_1 + M_2 f_2)}{d_{1,2}} - \frac{(\epsilon_1 - 1) M_1 f_1}{(\epsilon_1 + 2) d_1}\right\} \Big/ f_2$$

now proportionally changes by the factor $(\epsilon_{1,2} + 2)$ which itself varies with concentration in such a manner as to annul the variation with concentration of $P_{2\,(D.C.M.)}$. Thus the calculations on the basis of the new equation have revealed that the P_2 of a large number of halides and other normal compounds are independent of the concentration of the solvent. There are of course anomalies which, as will be elaborated elsewhere, find quantitative explanation on the basis of hindered rotation and preferred orientation. One anomaly which persists in Debye's equation, *viz.*, the occurrence of maxima and minima in the P_2 versus f_2 curves (*e.g.*, alcohols) is completely eliminated in the new equation.

Wyman[15] has shown that the linear dependence of dielectric constant with concentration observed in aqueous solutions of amino acids can be accounted for by the $(\epsilon - 1)$ law for polarisation. Hedestrand[8] has similarly observed that the dielectric constants of a series of solutions exhibit a linear dependence on concentration in dilute solutions. These observations can be explained on the basis of the new equation as follows:

Considering weight fractions $p_{1,2} = (\epsilon_{1,2} - 1/d_{1,2} = p_1\omega_1 + \omega_2 p_2 = p_1 + \overline{p_2 - p_1}\,\omega_2$. Substituting $d_{1,2} = d_1 (1 + \beta\,\omega_2)$, where $\beta =$ constant; $(\epsilon_{1,2} - 1) = d_1(1 + \beta\omega_2)\ (p_1 + \overline{p_2 - p_1}\,\omega_2)$ or $\epsilon_{1,2} = \epsilon_1 + d_1(p_2 - p_1 + \beta p_1)\,\omega_2 + \beta d_1\,(p_2 - p_1)\,\omega_2^{\,2}$.

If ω_2 is small $\epsilon_{1,2} = \epsilon_1 + K\omega_2$ (K being a constant).

Considering mol fractions $P_{1,2} = \dfrac{(\epsilon_{1,2} - 1)(M_1 f_1 + M_2 f_2)}{d_{1,2}}$ $= P_1 f_1 + P_2 f_2 = P_1 + (P_2 - P_1) f_2$. Putting $d_{1,2} = d_1 (1 + \gamma f_2)$, where $\gamma =$ constant

$$(\epsilon_{1,2} - 1) = \frac{P_1 d_1 + [(P_2 - P_1) d_1 + \gamma P_1 d_2] f_2 + \gamma (P_2 - P_1) d_1 f^2_2}{M_1 + (M_2 - M_1) f_2}$$

Since $M_1 >> (M_2 - M_1) f_2$, $\epsilon_{1,2} = \epsilon_1 + K' f_2 + K'' f_2^2$, K' and K'' being constants. If f_2 is small $\epsilon_{1,2} = \epsilon_1 + K' f_2$.

Wyman[16] has observed that in the case of glycine and other amino acids the dielectric increment, which is defined as $\frac{(\epsilon_{solution} - \epsilon_{solvent})}{\text{mols/litre of solute}}$, is independent of the dielectric constant of the solvent used. This directly follows from the new equation as follows. It has been deduced above that $\epsilon_{1,2} = \epsilon_1 + d_1 (p_2 - p_1 + \beta p_1)\, \omega_2$ when ω_2 is small; in other words, $(\epsilon_{1,2} - \epsilon_1)/\omega_2$ which is proportional to the dielectric increment as defined by Wyman, $= d_1 (p_2 - p_1 + \beta p_1)$. Since it has been found that the specific polarisation p_2 of the solute in the case of these amino acids is very much higher than the p_1 of solvent, any change in p_1 (*i.e.*, in the dielectric constant of the solvent used) produces a negligible effect on the value $p_2 - p_1 + \beta p_1$, *i.e.*, on the dielectric increment. It is obvious that when the dielectric constant of the solvent is comparable to that of the solute the dielectric increment would fall with increase in dielectric constant of the solvent. Such decrease has been observed[16] in the case of 'α' amino-butyric acid when 'δ' falls from 24 to 18 as $\epsilon_{solvent}$ increases from 35 to 134. When the dielectric constant of the solvent is, on the other hand high compared with that of the solute then it is possible that the factor $p_2 - p_1 (1 - \beta)$ becomes negative (since p_2 is less than p_1) which means that δ can be negative. In fact such negative increments have been observed by Devoto and others.

Kirkwood has generalised Onsager's theory to include dielectric homogeneity of the medium in the vicinity of the molecule due to the hindering of rotation of its neighbours by the molecules, and has derived for the dielectric polarisation

$$\frac{(\epsilon - 1)\ (2\epsilon + 1)}{9\epsilon}\frac{M}{d} = P_E + P_a + \frac{4\pi}{3}\frac{N\mu^2 g}{kT},$$

where g is a parameter whose value differing from unity is a measure of the hindering effect of a molecule. Extending the equation to solutions Oster[13] has found that the parameter 'g' evaluated from the observed values of the dielectric constant and density data of solutions using the indicated gaseous dipole moments to calculate μ_{soln}. by Onsager's relation

$$\mu_{soln} = \frac{2\epsilon_{soln} + 1}{2\epsilon_{soln} + n_2^2}\frac{n_2^2 + 2}{3}\ \mu_{gas}$$

is a function of both temperature as well as the concentration of the solute. The 'g' versus concentration curves are anomalous and are accompanied in many cases by minima. These deviations have not been accounted for in a quantitative manner but are qualitatively attributed to molecular association. Using the equation $(\epsilon + 1)(2\epsilon + 1)/9\epsilon$ for polarisation, Oster evaluated the dielectric increment of alcohols, acetone and other pure liquids in dilute aqueous solutions, and found that the calculated increments were in agreement with the observed. His expression for δ was given as

$$`\delta\text{'}_{\text{Oster}} = \left[\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{2\epsilon_2} - (\epsilon_1 - 1)\right]\frac{V_2}{1000}$$

where V_2 = molar volume of the solute. If however, the $(\epsilon - 1)$ law is used, 'δ' is given by $\delta_{\text{new}} = [\epsilon_2 - \epsilon_1]\, V_2/1000$. When $\epsilon_2 >> 1$ (as is usually for polar liquids) it is seen that Oster's expression coincides with δ_{new} and hence the apparent identity of $\delta_{\text{calculated}}$ and δ_{observed} is fortuitous.

Hedestrand[8] as well as Le Fevre and Vine[10] have derived an equation to calculate without graphical extrapolation $P_{2(\infty)}$, the polarisation at infinite dilution of the solute. These equations are derived by substituting the observed linear relationship between the dielectric constant of solution and the concentration of solute in the classical Clausius-Mosotti expression for polarization. Such a substitution is improper since on the basis of the Clausius-Mosotti expression it is not possible to explain the linear dielectric increment in dilute solutions. The correct expression for $P_{2(\infty)}$ is however got by using the $(\epsilon - 1)$ law for polarisation which, as has been shown previously, explains the linear dielectric increment. Since $\epsilon_{1,2} = \epsilon_1 (1 + a\omega_2)$....(1) and $d_{1,2} = d_1 (1 + \beta\omega_2)$ .... (2), where a and β are constants and ϵ_1, d_1 the dielectric constant and density of the solvent;

$$p_{1,2} = p_1\omega_1 + p_2\omega_2 \text{ or } p_2 = \frac{p_{1,2} - p_1\omega_1}{\omega_2} = p_{1,2} + \frac{\omega_1}{\omega_2}(p_{1,2} - p_1)$$

$$= \frac{\epsilon_{1,2} - 1}{d_{1,2}} + \frac{\omega_1}{\omega_2}\left[\frac{\epsilon_1(1 + a\omega_2) - 1}{d_{1,2}} - \frac{(\epsilon_1 - 1)(1 + \beta\omega_2)}{d_{1,2}}\right]$$

using the equations (1) and (2). In the limiting case of infinitely dilute solution, *i.e.*, when $\omega_2 \rightarrow 0$; $\omega_1 \rightarrow 1$, $\epsilon_{1,2} \rightarrow \epsilon_1$ and $d_{1,2} \rightarrow d_1$ and hence

$$p_{2(\infty)} = \frac{(\epsilon_1 - 1)}{d_1} + \frac{1}{d_1}\left\{\epsilon_1 a - \overline{\epsilon_1 - 1}\,\beta\right\}$$

$$= \frac{(\epsilon_1 - 1)}{d_1}(1 - \beta) + \frac{\epsilon_1 a}{d_1}$$

as compared with the equation derived by Le Fevre and Vine

$$p_{2(\infty)} = \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}\frac{(1 - \beta)}{d_1} + \frac{\epsilon_1 a}{d_1}\cdot\frac{3}{(\epsilon_1 + 2)^2}\cdot$$

Norman C. C. Li and Ting-Li Chu[11] in a recent paper have pointed out that the above relationship is advantageous in that a knowledge of the molecular weight of the solvent is not necessary in calculating the molar polarisation and dipole moment of the solute. It is to be pointed out here that Sugden's[14] equation involving specific polarisations and weight fractions provides even a simpler method of calculating the dipole moment of the solute without knowing the molecular weight of the solvent. In view of this fact it is evident that Le Fevre and Vine's equation has no special advantage as claimed by Norman C. C. Li and Ting-Li Chu. Apart from this, the derivation of the Le Fevre and Vine's equation itself is erroneous in that it involves the substitution of a linear relation between dielectric constants and concentration in the Clausius-Mosotti equation on the basis of which the linearity of dielectric constants cannot be explained. The moment derived by Le Fevre and Vine's equation bears the ratio of 1·4 (approx.) to that calculated by the corresponding expression derived by using the correct law of polarisation $(\epsilon - 1)\,M/d$ in place of the Clausius-Mosotti expression $(\epsilon - 1)\,M/(\epsilon + 2)\,d$.

SUMMARY

The experimental verification of the previous theories of Debye in the case of dilute solutions and of Onsager, Frolich and Sack and Wyman for pure liquids has been found to be due to remarkable and fortuitous coincidence which arises from the fact that their equations arithmetically approximate to the correct relationship $(\epsilon - n^2)\,M/d = 4\pi N\mu^2/kT$. In solutions the anomalous variation of (D.C.M.) polarisation with concentration is rectified by using the new equation. The linear dependence of dielectric constant with concentration, observed in dilute solutions by Wyman, Hedestrand and others is explained on the basis of the new equation. The derivation of Le Fevre and Vine's relationship for the polarisation at infinite dilution has been shown to be inconsistent and has been modified by using the new relationship.

ACKNOWLEDGMENT

Thanks of the authors are due to the Council of Scientific and Industrial Research for financial assistance for this research.

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986-48 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent